

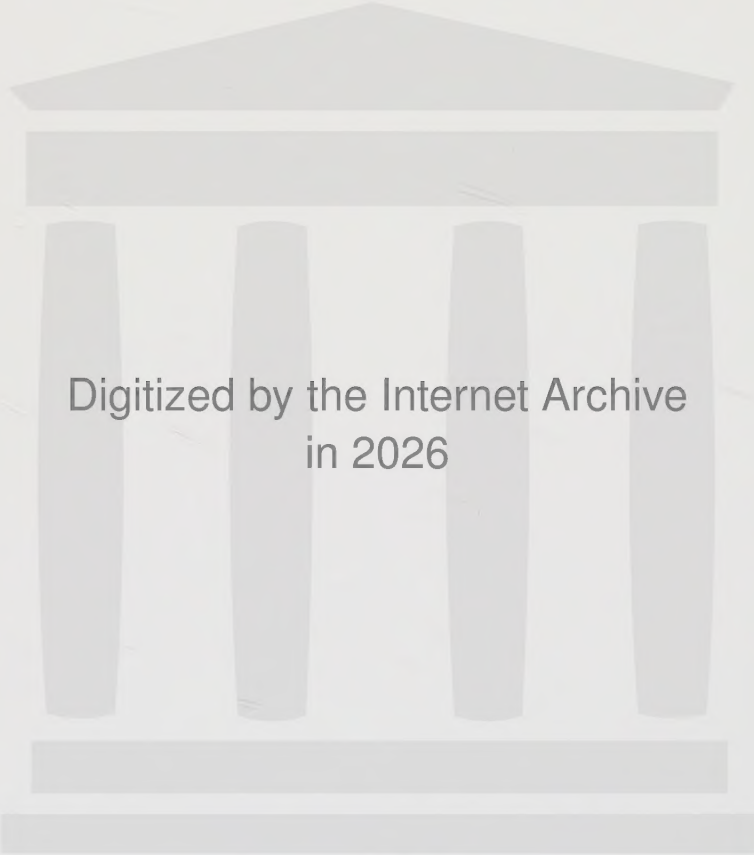
HYDROTHERMAL EXPERIMENTS WITH MAGNESIUM-CHLORITE AND SOME IDEAS FOR A NEW BUFFER TECHNIQUE

by

E. TORBJÖRN WIDMARK



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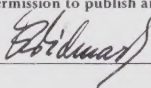
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Title and subtitle Hydrothermal experiments with magnesium-chlorite and some ideas for a new buffer technique			
Abstract Recent estimations, based on investigations of mineral paragenesis in field, suggest a greater stability of magnesium-chlorite than expected from thermodynamic calculations. With conventional hydrothermal equipment, the reaction magnesium-chlorite+dolomite=spinel+forsterite+calcite+fluid has been investigated and new thermodynamic data for magnesium-chlorite retrieved. These new data ($\Delta H_f = -8843937$ J/mole, $\Delta S_f = -2184,38$ J/mole $^{\circ}$K) are in better agreement with field evidence. With present hydrothermal experimental technique, the calculated position of an invariant point in an isobaric T-X diagram is often uncertain. With a new experimental set-up, called 'interstratified buffering', the position of an invariant point can be experimentally determined and thermodynamic calculations performed on all univariant reactions radiating from it. If certain pre-conditions are fulfilled, then the 'interstratified buffer' technique will be a useful complement in retrieving consistent thermodynamic data.			
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AND SOME IDEAS FOR A NEW BUFFER TECHNIQUE

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E. Torbjörn Widmark

Translation supervised by Mr. C. Montagu-Evans (Cantab.)

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Naturvetenskapliga Forskningsrådet

DEDICATED TO
MY FAMILY AND PARENTS
EVA OLOF ERIK
DAISY PER HENRIK
AND TO
SCIENCE
GUIDED BY
LOVE, CURIOSITY AND HUMANITY



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The Reaction

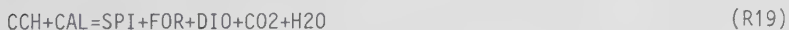
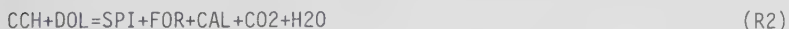
chlorite+dolomite=spinel+forsterite+calcite+carbon dioxide+water

Abstract

The reaction chlorite+dolomite=spinel+forsterite+calcite+CO₂+H₂O has been studied with hydrothermal equipment in a C-O-H fluid at $P_{\text{fluid}}=1000, 2000$ and 3000 bar and f_{O_2} controlled by NB or QFM buffer. The equilibrium conditions for the reaction has been determined as $\log K = -57119/T + 95.77 + 0.9860(P-1)/T$ (bar, K). The mineral mixtures had an excess of dolomite. The composition of the chlorite among the reaction products has been analysed and found to have a higher Al/Si ratio than clinochlore.

Introduction

Magnesium-chlorite occurs as a typical and widespread constituent of low to medium grade metamorphosed impure dolomites. At higher metamorphic grades magnesium-chlorite becomes unstable relative to various magnesium-spinel assemblages (Bucher 1977; Rice 1977). The two principal reactions describing the upper stability limit of magnesium-chlorite with dolomite and calcite in CO₂-H₂O fluids are



(Explanations of symbols and abbreviations in Table 1). Due to large uncertainties in the experiment of Fawcett and Yoder (1966) thermodynamic data for clinochlore are uncertain (Zen 1972; Chernosky 1974). Calculated isobaric T-X_{CO₂} sections for chlorite-spinel equilibria in carbonate rocks suffer from these uncertainties as well and are partly inconsistent with field observations (Bucher 1977) on chlorite-spinel marbles. A direct determination of the equilibrium conditions for reaction (R2) therefore promised to narrow down the

uncertainties in the phase diagram for low pressure metamorphism of chlorite bearing dolomites.

Experimental methods

The experiments were conducted in Nimonic 105, cold seal pressure vessels of Tuttle (1949) type, heated externally in horizontal furnaces. The temperature was measured with chromel-alumel thermocouples calibrated against the melting points of antimony and zinc. The thermocouples were in contact with the samples during the run. The temperature, including the gradient along the sample and the variation during the run, is believed to be within 5°C of cited values. The pressure was measured on a factory calibrated Heise 7 kb precision manometer and the accuracy is believed to be ± 20 bar. Qualitative analyses of reaction products were made with the X-ray diffraction method and quantitative analyses of synthetic chlorites were made on a microprobe with EDX system and ZAF correction. During the run the composition of the C-O-H fluid was controlled with the buffering technique developed by Eugster (1957) and used by Skippen (1971). The NB and QFM buffers have been prepared using chemicals p.a. and the fayalite and magnetite synthesised from ferrous oxalate and Fe_2O_3 respectively (Skippen 1967). Quenching of the autoclaves was made with a high power fan, lowering the temperature from 650°C to 200°C in less than 7 min.

Two different mixtures were used and the materials were mixed in proportions to give excess dolomite in the high temperature assemblage.

A. Hydroxides, oxides and carbonates p.a.

B. Synthetic forsterite, synthetic spinel, CaCO_3 and MgO p.a.

Reaction products from mixture A were reused in later runs. To the mixtures 3-5% spectrographically pure graphite were added. The mixtures, together with a mixture of oxalic acid and silver oxalate, were welded in an inner gold capsule which were put in an outer gold

or silver-palladium capsule containing the oxygen buffer, NB or QFM respectively. After the hydrothermal run, the oxygen buffer was checked with the X-ray diffraction method. The oxalic acid - silver oxalate mixtures were of three different types to give an initial CO₂-H₂O fluid with X_{CO_2} = 0.50, 0.67 and 0.78.

Composition of chlorite and stoichiometry of reaction

Some hydrothermal runs have been made with natural chlorite and dolomite with the composition $(\text{Mg}, \text{Fe}^{2+})_{5.1}(\text{Al}, \text{Fe}^{3+})_{0.9}\text{Si}_{3.1}\text{Al}_{0.9}\text{O}_{10}(\text{OH})_8$ and $\text{Ca}(\text{Mg}_{0.94}\text{Fe}_{0.03}\text{Mn}_{0.03})(\text{CO}_3)_2$ respectively. Using this mixture it can be clearly seen on the X-ray diffractograms that on approaching the reaction curve from the low temperature side, the chlorite reacts with dolomite to form a more aluminous chlorite together with forsterite and calcite before the reaction boundary is reached and formation of spinel is started (Fig. 1).

Run products with chlorite were dispersed in epoxy glue and analysed on the microprobe. Because of the extremely small grain size, the electron beam could not be focused on chlorites. Using very low beam current, analyses were made from small surfaces of epoxy glue and chlorite. If the total sum of MgO, Al₂O₃ and SiO₂ exceeded 49%, the analyses were accepted and normalized on the basis of 14 oxygens (Table 2). The average 'break down' composition of synthetic chlorite is:

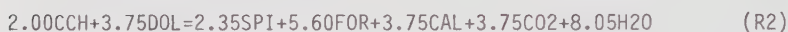
	$\bar{X}$	s
Si	2.78	0.119
Al	2.37	0.180
Mg	4.88	0.160

These values are in excellent agreement with the composition of chlorites from natural chlorite-spinel assemblages (Table 3). 10 analyses of chlorite from the assemblage CCH-SPI-CAL-DOL-FOR (Bucher

1977; Rice 1977) and 3 analyses of chlorite from the assemblage CCH-SPI-ENS-FOR (Frost 1975) were recalculated and yield an average 'break down' composition of natural chlorite of

	$\bar{X}$	s
Si	2.80	0.052
Al	2.34	0.072
Mg	4.88	0.067

The composition $\text{Mg}_{4.90}\text{Al}_{2.35}\text{Si}_{2.80}\text{O}_{10}(\text{OH})_{8.05}$ has been used to calculate the stoichiometry of reaction (R2):



Construction of the $\log K$ versus $1000/T$ plot

For the calculation of the fugacities of gas species in the capsule the method used by Skippen (1967) has been used together with the following data:

NB buffer $\log f_{\text{O}_2} = -24930/T + 9.36 + 0.0458(P-1)/T$ (Huebner 1971)

QFM buffer $\log f_{\text{O}_2} = -23973/T + 7.99 + 0.0937(P-1)/T$ (Chou 1978)

$\log K_{\text{CO}_2} = 20586/T + 0.0421 + 0.0278(P-1)/T$

$\log K_{\text{H}_2\text{O}} = 12510/T + 0.483 - 0.979 \log T$

$\log K_{\text{CO}} = 5835/T + 4.577 + 0.0278(P-1)/T$ (linear combination)

$\log K_{\text{CH}_4} = 3609/T + 3.412 - 2.677 \log T + 0.0278(P-1)/T$ (linear combination)

(Ohmoto and Kerrick 1977)

In addition γ_i has been calculated from the equation $\gamma_i = D + E/T - G(1000/T - 1.1607)^2$. The D, E and G constants (Table 4) have been calculated to fit the γ_{CO_2} , $\gamma_{\text{H}_2\text{O}}$ of Skippen (1971) and γ_{CO} , γ_{H_2} , γ_{CH_4} of Ryzhenko and Volkov (1971). In the temperature interval 743 - 1003 K these calculated values are within 0.005 and 0.01 respectively of cited values. Ideal mixing in the fluid phase has been assumed.

In order to recalculate the 1000, 2000 and 3000 bar data to 1 bar reference state, the calculated buffer curves have been corrected with the relation $\log f_{P,T} = \log f_{1,T} - \frac{\Delta V_S(P-1)}{RT \ln 10}$ (Eugster and Wones 1962). For this purpose the molar volume of 'break down' chlorite has been calculated, 212.266 cm^3 , using the density 2.629 (Wetzel 1973) for magnesium-chlorite. This value together with volume data for the other phases (Table 1) in the reaction, gives (R2) a ΔV_{S2} of -188.762 cm^3 . After pressure correction of the buffer curves each hydrothermal run has been plotted on its respective buffer curve.

Results

The experimental results are listed in Table 5 and graphically shown in Fig. 2. In some samples the presence of a 7-A phase, probably a chlorite, was detected. When the 7-A phase was put under hydrothermal conditions for another 2-3 weeks, it disappeared under simultaneous growth of 14-A chlorite. This phenomenon has earlier been observed by Yoder (1952), Roy and Roy (1955), Fawcett and Yoder (1966) and Chernosky (1974). In this investigation the 7-A phase is considered to be metastably formed in the stability field of 14-A chlorite (Helgeson et al. 1978). Similarly the appearance of magnesite in the reaction products of the oxide mixture is considered to be metastable.

The reversibility of the reaction is demonstrated by the formation of chlorite from the mixture of synthetic forsterite and spinel and the formation of the unvariant assemblage CCH-SPI-CAL-DOL-FOR from the oxide mixture.

Using the expression

$$\log K_2 = 3.75 \log f_{\text{CO}_2} + 8.05 \log f_{\text{H}_2\text{O}} \equiv A/T + B + C(P-1)/T$$

$$(A = -\Delta H_R^0/R \ln 10, B = \Delta S_R^0/R \ln 10, C = -\Delta V_S/R \ln 10)$$

the B and C constants have been calculated using data according to Table 1.

$$C = -\Delta V_2 / R \ln 10 = 0.9860$$

$$B = \Delta S_2^0 / R \ln 10 = 95.77$$

The A constant was then calculated to give a reaction curve passing midway between sample 2362 and 2016 in Fig. 2.

$$\log K_2 = 32.6 = 1.106A/1000 + B, \quad A = -57119.$$

The equilibrium curve in Fig. 2 can thus be represented by

$$\log K_2 = -57119/T + 95.77 + 0.9860(P-1)/T.$$

Conclusions

The new experimental results expand the known stability of chlorite (Fig. 3) and might solve some of the discrepancies between experimental results discussed by Helgeson et al. (1978). The presently used thermodynamic data for cordierite and phlogopite have been calculated from reactions involving magnesium-chlorite. The new values for magnesium-chlorite given in this paper consequently necessitate the production of a new set of consistent thermodynamic data also for these minerals.

Acknowledgements

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Table 1

Constants and symbols. Standard state 298 K, 1 bar.

CAL	calcite	FOR	forsterite
CCH	chlorite	MAG	magnesite
DIO	diopside	SPI	spinel
DOL	dolomite	CO2	carbon dioxide
ENS	enstatite	H2O	water

ΔH_R^0 standard enthalpy change of reaction (R)

K_2 equilibrium constant of reaction (R2)

ΔS_R^0 standard entropy change of reaction (R)

ΔS_2^0 standard entropy change of reaction (R2)

ΔV_S volume change of solids of reaction (R)

ΔV_2 volume change of solids of reaction (R2)

f_i fugacity of species i

γ_i fugacity coefficient of species i

J joule (4.187 J/cal)

P pressure in bar

R gas constant 8.314

T temperature in K unless otherwise noted

Entropy value for chlorite from Chernosky (1974).

Molar volume of chlorite 212.266 cm³.

Other thermodynamic data from Helgeson et al. (1978).

Table 2. Microprobe analyses of synthetic 'break down' chlorite

Sample	2014	2310	2311	2312	2313	2318	2320	2321	2326a	2326b	2326c
SiO ₂	20.05	21.08	22.12	18.81	19.45	23.36	27.39	16.84	20.92	15.45	19.92
Al ₂ O ₃	14.27	15.09	15.46	13.03	12.59	20.41	17.43	11.77	13.84	13.85	15.11
MgO	22.84	25.28	25.08	22.69	20.20	27.71	31.46	21.11	25.25	19.89	23.49
Total	57.16	61.45	62.66	54.53	52.24	71.48	76.28	49.72	60.01	49.19	58.52
Cations per formula unit based on 14 oxygen											
Mg	4.79	4.95	4.80	5.01	4.62	4.66	4.95	5.12	5.07	4.88	4.82
Al	2.37	2.34	2.34	2.28	2.28	2.71	2.17	2.26	2.20	2.69	2.45
Si	2.83	2.77	2.84	2.79	2.98	2.64	2.90	2.74	2.82	2.54	2.75

Table 3. Natural 'break down' chlorites

	Rice (1977)				Frost (1975)				Bucher (1977)				
	48.1b	76b	77b	106a	179b	7	8	9	P7C1E1	P7C1E2	P42K1A1	P41A1C1	P41A1C2
Si, Ti	2.84	2.81	2.86	2.84	2.88	2.83	2.78	2.83	2.69	2.75	2.78	2.76	2.78
Al, Cr, Fe ³⁺	2.35	2.42	2.25	2.34	2.23	2.26	2.34	2.33	2.48	2.38	2.31	2.42	2.35
Mg, Fe ²⁺ , Mn, Ni	4.80	4.75	4.90	4.81	4.89	4.96	4.94	4.86	4.90	4.93	4.98	4.85	4.92

Table 4. Constants for calculation of fugacity coefficients (γ_i) in the temperature interval 743- 1003 K using the equation

$$\gamma_i = D + E/T - G (1000/T - 1.1607)^2$$

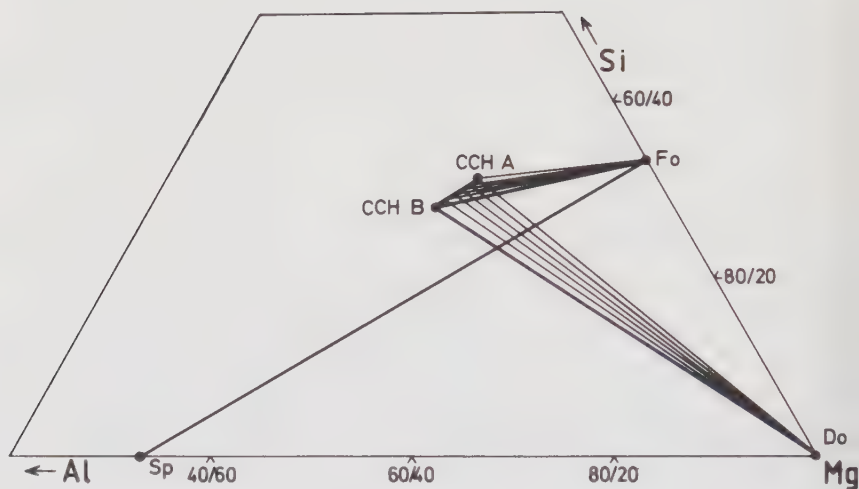
i		D	E	G
H2O	500	1.717630	- 815.307836	0.927639
	1000	1.938015	- 1139.475435	0.317909
	2000	1.861554	- 1168.056337	-0.543940
	3000	1.855170	- 1172.569111	-0.771434
CO2	500	1.307809	- 116.956060	0.170147
	1000	1.506631	- 132.750769	0.293931
	2000	1.809741	- 4.136710	0.876249
	3000	2.190999	449.397078	0.309177
CO	500	1.068707	125.981608	0.066962
	1000	1.028893	417.431595	0.221112
	2000	0.581958	1541.864450	0.543539
	3000	-0.313664	1346.974050	0.915638
H2	500	0.962465	141.024188	0.022772
	1000	0.898548	323.415470	0.053054
	2000	0.672721	834.863190	0.155616
	3000	0.318205	1538.103805	0.282308
CH4	500	1.108282	63.930965	0.055812
	1000	1.189256	229.399345	0.114282
	2000	1.264705	872.469640	0.417733
	3000	1.223720	1936.732175	0.859597

Table 5. Compilation of hydrothermal runs for reaction CCH+DOL=SPI+FOR+CAL+C02+H20

Sample number	P bar	T°C	Time days	Buffer	Present after run	Starting mixture
2013	1000	547	20	NB	CCH DOL	B
2014	3000	613	20	NB	CCH DOL	B
2016	3000	624	37	NB	CCH DOL	B
2023	2000	594	40	NB	CCH DOL	B
2015	3000	616	20	NB	CCH DOL	B
2310	1000	547	20	NB	CCH DOL	A
2317	3000	630	38	NB	CCH DOL SPI FOR CAL	A
2334	1000	565	28	NB	DOL SPI FOR CAL	A
2344	3000	656	15	QFM	DOL SPI FOR CAL	A
2351	1000	565	15	QFM	CCH DOL SPI FOR CAL	A(reused)
2358	1000	580	15	QFM	DOL SPI FOR CAL	A(reused)
2359	1000	580	15	QFM	DOL SPI FOR CAL	A(reused)
2362	3000	640	15	QFM	DOL SPI FOR CAL	A(reused)
2365	1000	545	30	NB	CCH DOL	A(reused)
2366	1000	545	30	NB	CCH DOL SPI FOR CAL	A(reused)
2368	1000	527	27	NB	CCH DOL SPI FOR CAL	A(reused)
2373	3000	618	14	NB	CCH DOL SPI FOR CAL	A(reused)
2374	3000	618	14	NB	CCH DOL SPI FOR CAL	A(reused)

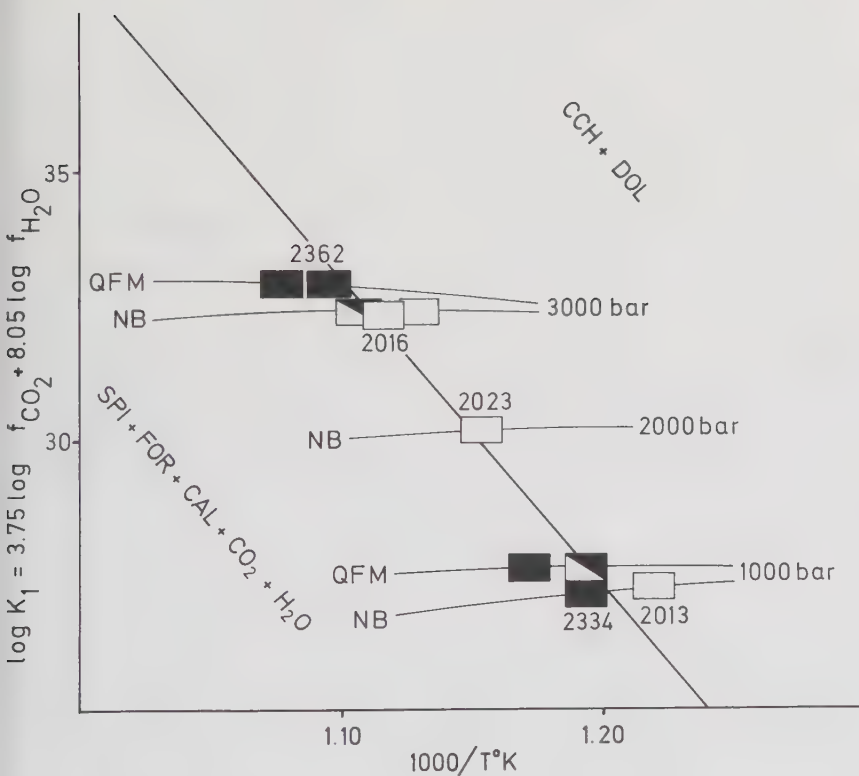
A(reused) containing the synthetic CCH-DOL-SPI-FOR-CAL-MAG-7-A. 7-A=7-A phase

Fig 1



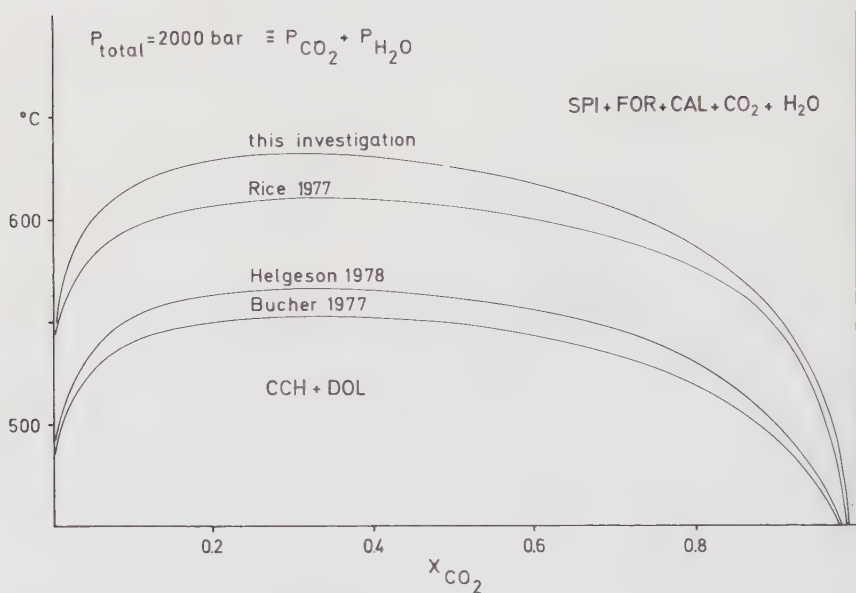
During low pressure prograde metamorphism a CCH A with low aluminium content reacts with DOL to produce FOR, CAL and a more aluminium rich CCH up to the point CCH B, where it decomposes and SPI-FOR-CAL becomes more stable relative to CCH-DOL. Projection from CAL, CO₂, H₂O corner.

Fig 2



log K versus 1000/T diagram with sections of pressure corrected buffer curves. Critical runs with estimated fields of uncertainty inserted and calculated reaction curve drawn.

Fig 3



Isobaric T - x_{CO_2} diagram with reaction curves from different authors for the reaction $\text{CCH} + \text{DOL} = \text{SPI} + \text{FOR} + \text{CAL} + \text{CO}_2 + \text{H}_2\text{O}$ at 2000 bar. The activities of calcite and magnesite fixed by the calcite-dolomite miscibility gap.

New thermodynamic data for magnesium-chlorite

Introduction

The wide occurrence of chlorite in nature, considering both variation in bulk chemistry and metamorphic grade, brings justified interest to this mineral. New hydrothermal experiments (Widmark 1980) show greater stability of magnesium-chlorite coexisting with dolomite, calcite, forsterite, spinel in a fluid of H₂O-CO₂ than expected from calculations with hitherto accepted data (Helgeson et al. 1978). This fact necessitates a revaluation of the thermodynamic data of magnesium-chlorite.

Based on the experiments of Widmark (1980), the following calculations are performed to give data consistent with the thermodynamic properties of other minerals published by Helgeson et al. (1978).

Abbreviations used. Standard state 298 K, 1 bar.

CAL	calcite
CCH	'break-down' chlorite
CCN	stoichiometric clinochlore
CH ₄	methane
CO	carbon monoxide
CO ₂	carbon dioxide
COM	corundum
DOL	dolomite
ENS	enstatite
FOR	forsterite
H ₂	hydrogen
H ₂ O	water

MAS	magnesite
QTZ	quartz
SPI	spinel

a,b,c	Maier-Kelley constants for Cp function
a_c^i	activity of component c in phase i
Cp^i	Maier-Kelley Cp function of phase i
ΔCp^R	Maier-Kelley Cp function of reaction (R)
f_i	fugacity of species i
γ_i	fugacity coefficient of species i
ΔG^R	experimentally determined free energy change of reaction (R) at P and T
ΔG_C^R	calculated free energy change of reaction (R) at P and T
ΔG_i	free energy of formation of phase i at P and T
ΔG_i^f	standard molar free energy of formation of phase i
ΔG_R^O	standard free energy change of reaction (R)
ΔH_i^f	standard molar enthalpy of formation of phase i
ΔH_R^O	standard enthalpy change of reaction (R)
K^{905}	equilibrium constant at 905 K
R	gas constant 8.324 J/mole,K
ΔS_i^f	standard molar entropy of formation of phase i
ΔS_R^O	standard entropy change of reaction (R)
V_i	molar volume of phase i
ΔV_S	volume change of solids in reaction

Calculations

The composition of 'break down' chlorite (Widmark 1980) has been slightly adjusted. In a triangular Mg-Al-Si diagram a tschermakitic exchange line passing through stoichiometric clinocllore has been constructed. The mean value of analysed natural 'break down' chlorites (Widmark 1980) has been projected orthogonally onto the exchange line. The adjusted composition is $\text{Mg}_{4.83}\text{Al}_{2.34}\text{Si}_{2.83}\text{O}_{10}(\text{OH})_8$. Based on this assumption the ΔS_i^f , a_i , b_i and c_i (Maier-Kelley Cp function) for CCH have been calculated (Helgeson et al. 1978).

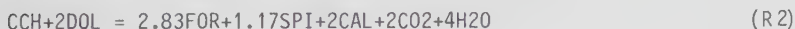
$$\Delta S_{\text{CCH}}^f = S_{\text{sum}}^0 (V_{\text{sum}} + V_{\text{CCH}}) / 2V_{\text{sum}} \quad \text{where} \quad (1)$$

$$S_{\text{sum}}^0 = \Delta S_{\text{CCN}}^f + 0.17\Delta S_{\text{COM}}^f - 0.17\Delta S_{\text{ENS}}^f \quad \text{and} \quad (2)$$

$$V_{\text{sum}} = V_{\text{CCN}} + 0.17V_{\text{COM}} - 0.17V_{\text{ENS}} \quad \text{and} \quad (3)$$

for the Cp function the a, b, and c constants have been calculated by substituting ΔS_i^f in expression (1) and (2) for a, b or c, respectively.

Using these new values for CCH the ΔV_s , ΔS_R^0 , Δa , Δb and Δc of the reaction



have been calculated.

Based on previous experimental results and reasoning (Widmark, 1980), the reaction curve is considered to pass midway between sample 2016 and 2362 in a $\log K$ versus $1000/T$ plot, giving an equilibrium temperature of 905 K at 3000 bar and a $\log K^{905} = 2\log f_{\text{CO}_2} + 4\log f_{\text{H}_2\text{O}} = \frac{1}{2}(\log K^{913} + \log K^{897})$ where $f_i = X_i^P \gamma_i$.

In order to make these new data consistent with the data of Helgeson et al. (1978), γ_i for CO_2 and H_2O have been calculated using the MRK equation (Holloway 1977) without the appropriate correction

(Flowers 1979), whereas γ_i (for $i = \text{CO}$, CH_4 and H_2) has been calculated according to Widmark (1980). After this, the calculation of the fugacities of gas species in the buffered capsule has been in accordance with the method previously used by Skippen (1967).

In order to correlate theoretically calculated and experimental data, the calculated free energy change of reaction (R2) has to be transformed from a DOL-CAL to a MAS component basis. Then this calculated free energy change of (R2) has to be corrected for the activity of the magnesite (Gordon & Greenwood 1970; Skippen 1974).

Thus for equilibrium we have

$$\Delta G_{\text{C}}^{\text{R2}} = \Delta G_{\text{C}}^{\text{R2}} + 2\Delta G_{\text{C}}^{\text{R20}} - 2RT \ln a_{\text{MAS}}^{\text{CAL}} \quad (4)$$

where

$$\text{MAS} + \text{CAL} = \text{DOL} \quad (\text{R20})$$

$$\begin{aligned} \Delta G_{\text{C}}^{\text{R2}} = & 2.83G_{\text{FOR}} + 1.17G_{\text{SPI}} + 2G_{\text{CAL}} + 2G_{\text{CO2}} + 4G_{\text{H2O}} - G_{\text{CCH}} - 2G_{\text{DOL}} + \\ & + RT \ln f_{\text{CO2}}^2 + RT \ln f_{\text{H2O}}^4 \end{aligned} \quad (5)$$

$$\Delta G_{\text{C}}^{\text{R20}} = G_{\text{DOL}} - G_{\text{MAS}} - G_{\text{CAL}} \quad (6)$$

and

$$\Delta G_i = \Delta H_i^f + \int_{298}^T C_p^i dT - T(\Delta S_i^f + \int_{298}^T \frac{C_p^i}{T} dT) + \int_1^P V_i dP \quad (7)$$

For fluid components the term $\int_1^P V_i dP$ is substituted with $RT \ln f_i$.

$$\text{After approximating } \int_1^P V_i dP = V_i(P-1) \text{ for solids and defining} \quad (8)$$

$$A = -(\Delta H_{\text{R2}}^0 + \int_{298}^T \Delta C_p^{\text{R2}} dT) / R \ln 10 \quad (9a)$$

$$B = (\Delta S_{\text{R2}}^0 + \int_{298}^T \frac{\Delta C_p^{\text{R2}}}{T} dT) / R \ln 10 \quad (9b)$$

and

$$C = -\Delta V_S^{R2}/R \ln 10 \quad (9c)$$

we obtain the expression for equilibrium of the unvariant reaction (R2):

$$2\log f_{CO2} + 4\log f_{H2O} + 2 \frac{\Delta G_C^{R20}}{R \ln 10} - 2\log a_{MAS}^{CAL} =$$

$$= A/T + B + C(P-1)/T \quad (10)$$

In this expression

$$\log a_{MAS}^{CAL} = -\frac{731}{T} + 0.4854 \quad (\text{Gordon \& Greenwood, 1970}) \quad (11)$$

and

$$\Delta G_C^{R20}/R \ln 10 = \frac{535}{T} + 0.1664 + \frac{0.0032(P-1)}{T} \quad (12)$$

(calculated with data from Helgeson et al. (1978))

Inserting calculated and experimentally determined values at equilibrium temperature 905 K into the expression (10), makes it possible to determine ΔH_{CCH}^f and owing to the relation

$$\Delta G_i^f = \Delta H_i^f - 298\Delta S_i^f \quad (13)$$

the standard free energy of formation of CCH is also given.

Conclusion

These new thermodynamic data for 'break-down' chlorite (Table 6) expand the calculated stability field (Fig. 4) and change the topology in the $T-X_{CO2}$ diagram. This diagram is supported by previous estimations (Rice 1977) and observed sequences of parageneses in nature (Bucher 1977).

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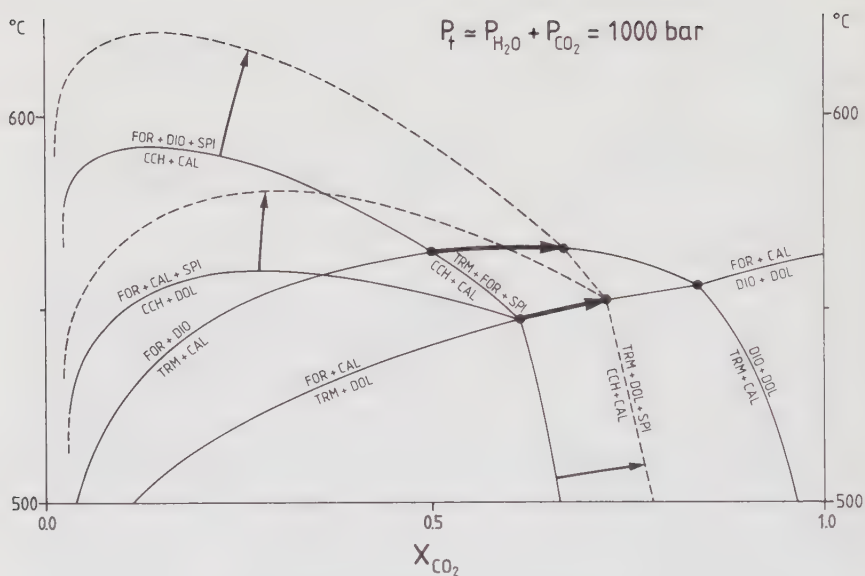
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Table 6

Thermodynamic data (joule, mole, K, bar, standard state 298 K, 1 bar)

	ΔG_i^f	ΔH_i^f	ΔS_i^f	V_i	a_i	b_i	c_i	reference
CAL	-1130098	-1208222	-262.028	3.6934	104.5163	0.021924	-2594080	Helgeson et al. 1978
CCH	-8192665	-8843937	-2184.377		699.3141	0.174927	-15840111	this paper
CCN			-2178.809		696.6360	0.176146	-15677448	Helgeson et al. 1978
CCH				21.0487				Hey 1954
CCN				21.1103				Hey 1954
C02	-394392	-393522	2.919		44.2249	0.008786	-861904	Helgeson et al. 1978
COM	-1568264	-1661655	-313.235	2.5575	115.0182	0.011799	-3506192	Helgeson et al. 1978
D0L	-2167228	-2329865	-545.485	6.4340	173.8745	0.100215	-4135466	Helgeson et al. 1978
ENS	-1459923	-1546766	-291.273	3.1276	102.7172	0.019832	-2627552	Helgeson et al. 1978
F0R	-2056704	-2175680	-399.048	4.3790	149.8290	0.027363	-3564768	Helgeson et al. 1978
H2O	-228589	-241818	-44.373		30.5432	0.010293		Helgeson et al. 1978
MAS	-1027833	-1111396	-280.371	2.8018	82.5545	0.052463	-1986563	Helgeson et al. 1978
QTZ	-856239	-910648	-182.488	2.2688	46.9445	0.034309	-1129680	Helgeson et al. 1978
SPI	-2163153	-2288008	-418.765	3.9710	153.8582	0.026840	-4062246	Helgeson et al. 1978

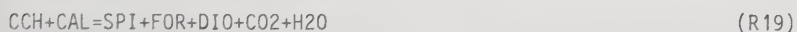
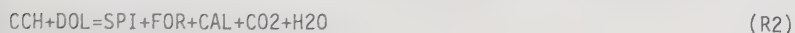
Fig 4



Isobaric T-X diagram showing displacement of reaction curves and invariant points due to new experimental data. Dashed curves calculated with new thermodynamic data for 'break down' chlorite.

Hydrothermal experiments: the reaction
 chlorite+dolomite=spinel+forsterite+calcite+fluid
 and ideas for a new buffer technique.

In metamorphosed impure marbles, magnesium-chlorite is a common constituent. At higher metamorphic grades, this chlorite becomes metastable relative to various magnesium-spinel assemblages. Two principal reactions describing the upper stability limit of magnesium-chlorite with dolomite and calcite in CO₂-H₂O fluids are



(explanations and symbols in Table 7). Due to uncertainties in and lack of data from earlier experiments with magnesium-chlorite (Fawcett & Yoder 1966), calculated T-X_{CO₂} sections for chlorite-spinel equilibria in carbonate rocks have been unreliable and partly inconsistent with field observations (Bucher 1977). An investigation of reaction (R2) (Widmark 1980) has presented new data, drastically changing the topology of chlorite reactions in T-X_{CO₂} sections (Fig. 5).

For instance, the invariant point II is moved from X_{CO₂}=0.25, 545°C to X_{CO₂}=0.80, 565°C at 1000 bar fluid pressure. This later value agrees well with estimates by Rice (1977).

Another interesting point concerning the topology in Fig. 5 is the displacement of invariant point III with changing pressure. Whereas the data of Skippen (1974) push the invariant point towards higher X_{CO₂} values with increasing pressure, the results of Käse & Metz (1980) show decreasing X_{CO₂} values with increasing pressure. The exact location of an invariant point is difficult to determine by present experimental techniques. As it is now, the location of a reaction curve is either determined by a gravimetric method (Metz 1976; Slaughter et al. 1975) or by the oxygen buffer technique (Skippen 1971).

In $T-X_{CO_2}$ diagrams, where two investigated reactions intersect at a low angle, the location of the invariant point is very uncertain (Slaughter et al. 1975), and the validity of the oxygen buffer technique has been recently held in question (Ziegenbein & Johannes 1980). Against this background the present paper discusses some ideas regarding a new buffer technique, which is named 'interstratified' buffering. This idea of the new technique and its designation are derived from Nature, where the composition of a fluid in a thin layer is controlled by reactions in the surrounding rocks.

The experimental set-up comprises of two mineral mixtures, for example

MIX_{12} representing the univariant mineral assemblage of reaction (R12) in Table 7 and

MIX_4 representing the univariant mineral assemblage of reaction (R4) in Table 7 where

$$\left| \frac{dT}{dX_{CO_2}} \right|_{MIX_4} \ll \left| \frac{dT}{dX_{CO_2}} \right|_{MIX_{12}}$$

In the experimental double capsule system, a small amount of MIX_4 is surrounded by a large amount of MIX_{12} (Fig. 6). If we put the system under hydrothermal conditions where the univariant assemblage of reaction (R12) is stable, this paragenesis will impose a certain fugacity of H_2O and CO_2 on MIX_4 (fugacities gravimetrically determined after the run) and make the coexistence of TRM+DOL impossible. In a series of experiments with successively lower temperatures, a point is reached where FOR+CAL and hence the univariant parageneses of reaction (R12) are metastable in the fluid. This is then the first 'bracket' of the invariant point I. Repeating the procedure at another pressure gives the second 'bracket'. These two 'brackets' make it possible to calculate the values of $\log K = A/T+B+C(P-1)/T$, not only

for reactions (R4) and (R12), but for all the univariant reaction curves originating from the invariant point.

The feasibility of using the 'interstratified' buffering technique is dependent on certain factors, which must be controlled or estimated by various methods. These include the following aspects:

1. The reaction kinetics of reactions used must be favourable.
2. There must be control of the compositions of the phases participating in the reactions to be able to determine the stoichiometric coefficients and activities.
3. The possibility of calculating the fugacity of H₂O and CO₂ in H₂O-CO₂ mixtures must be ensured.
4. There must be a way to determine the relative amounts of H₂O and CO₂ in the experimental fluid.

In addition to these factors, common to other hydrothermal experimental techniques, the following aspects have to be considered when using the 'interstratified' buffer:

5. There must be a sufficiently large amount of the controlling mix (in this case MIX₁₂ in relation to MIX₄) and favourable reaction kinetics in that mix to ensure that the controlling reaction (in this case (R12)) outruns the controlled mix (MIX₄ in this case).
6. There must be control of the diffusion rate of components between the two systems (in this case the regions occupied of MIX₁₂ and MIX₄).

This new technique of 'interstratified' buffering may solve, if the above preconditions are satisfied, some of the problems of locating invariant points in T versus X_{CO_2} diagrams.

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Table 7

Abbreviations, symbols and reactions

CAL	calcite	FOR	forsterite
CCH	chlorite	H ₂ O	water
CO ₂	carbon dioxide	SPI	spinel
DIO	diopside	TRM	tremolite
DOL	dolomite		

I,II and III invariant points in Fig. 5.

MIX₄ mixture of phases of reaction (R4) in stoichiometric proportions

MIX₁₂ mixture of phases of reaction (R12) in stoichiometric proportions

Non stoichiometric expressions of reactions shown in Fig. 5.

(R1) reaction $DIO + DOL = FOR + CAL + CO_2$

(R2) $CCH + DOL = SPI + FOR + CAL + CO_2 + H_2O$

(R4) $TRM + DOL = FOR + CAL + CO_2 + H_2O$

(R5) $TRM + CAL = DOL + DIO + CO_2 + H_2O$

(R6) $TRM + CAL = FOR + DIO + CO_2 + H_2O$

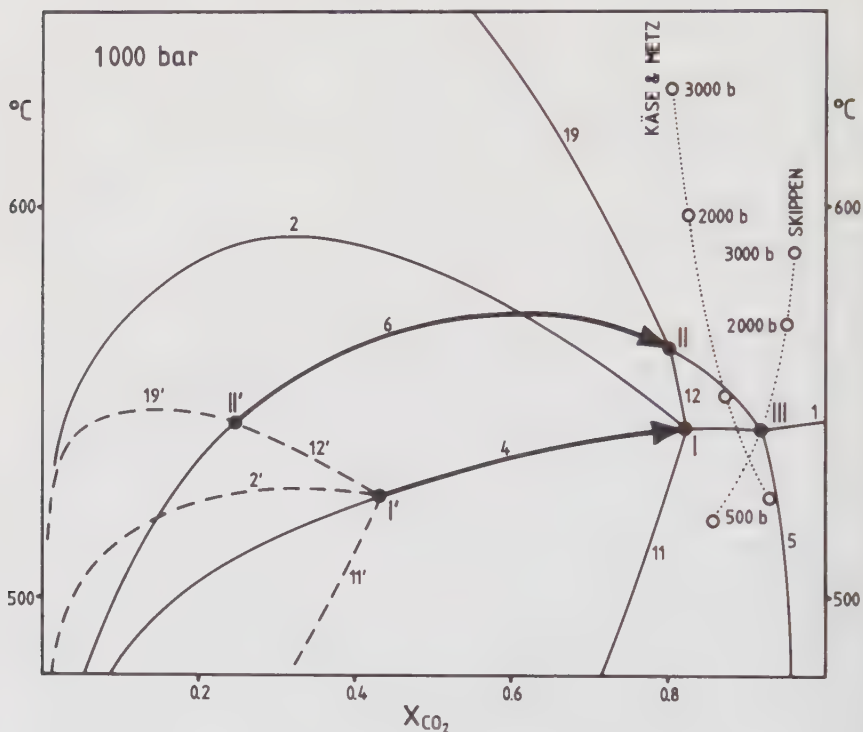
(R11) $TRM + DOL + SPI + H_2O = CCH + CAL + CO_2$

(R12) $CCH + CAL = SPI + TRM + FOR + CO_2 + H_2O$

(R19) $CCH + CAL = SPI + FOR + DIO + CO_2 + H_2O$

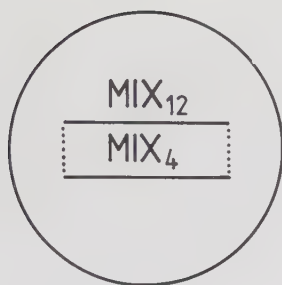
Primed reaction and invariant points in Fig. 5 refer to corresponding reaction curves presented by Bucher (1977).

Fig 5



Isobaric T-X_{CO2} section showing the change of topology as a result of new hydrothermal experiments with magnesium-chlorite and the displacement of invariant point III with changing pressure as a result of different experimental techniques. Primed reactions and invariant points show data from Bucher (1977).

Fig 6



Experimental set-up of capsules in the 'interstratified' buffering technique, showing outer sealed capsule and inner open capsule.

Thermodynamic data from experimentally determined invariant points in P-T-X space.

Abstract

As a complement to buffering techniques hitherto used in experimental petrology, a new 'interstratified buffering' was recently suggested. This method makes it possible not only to determine single reaction boundaries but also permits direct determinations of invariant points in P-T-X space and isobaric T-X sections. Thus, the relative thermodynamic properties of all reaction surfaces emanating from the invariant point may be fixed. This paper deals with the conditions for and procedure of retrieving thermodynamic data from a determined invariant point and the calculations involved.

Introduction

In hydrothermal experiments the fugacity of gas species has been mainly determined gravimetrically (Metz 1976; Slaughter et al. 1975) or has been controlled by oxygen buffers (Eugster & Wones 1962; Skippen 1971) or argon-hydrogen pressure systems (Shaw 1963). Recently, a new 'interstratified buffer' technique was suggested (Widmark 1981), which promises to be a satisfactory complement. The idea behind the new method is to determine the position of invariant points in P-T-X space or isobaric T-X sections, directly from hydrothermal experiments, thus making it possible to perform thermodynamic calculations on all reactions emanating from the invariant point. The present paper is a follow-up of the writers previous publication (Widmark 1981).

Abbreviations and symbols used

a_i	activity of i
C	number of components
ΔC_p^R	Maier-Kelley C_p function of reaction (R)
F	degree of freedom
f_i	fugacity of species i in fluid phase
ΔG_R^{TP}	free energy change of reaction (R) at P and T
ΔH_i^f	molar enthalpy of formation of phase i at 298 K, 1 bar
ΔH_i^T	molar enthalpy of formation of phase i at P and T
ΔH_R^T	enthalpy change of reaction (R) at P and T
K_R^{PT}	equilibrium constant of reaction (R) at P and T
n_i	stoichiometric coefficient of phase i
p	number of phases
R	gas constant
r	number of reactions
ΔS_i^f	molar entropy of formation of phase i at 298 K, 1 bar
ΔS_i^T	molar entropy of formation of phase i at P and T
ΔS_R^T	entropy change of reaction (R) at P and T
T_0	standard temperature 298 K
ΔV_R	volume change of solids in reaction (R)

Calculations

In a C component system we have located an invariant point at $P_1 T_1 X_1$ and $P_2 T_2 X_2$, with r univariant reactions radiating from the point. As a condition for the following reasoning and calculations we presume that:

I The C_p function for all participating phases is known or may be

estimated with reasonable accuracy. Used over a limited P-T-X space, a minor deviation from the correct Cp-function will not drastically change the results.

- II If not working with pure solids ($a_i=1$ and hence $RT \ln a_i=0$), we are able to estimate or calculate the activities of the solid solutions.
- III The molar volumes of all participating minerals are known.
- IV The fugacities of fluid species can be calculated. Although the fugacities of H₂O - CO₂ mixtures at various P-T-X conditions are difficult and time-consuming to determine, and the results sometimes questioned, there are theoretical ways of calculating these fugacities from the MRK-equation of state (Holloway 1977; Flowers 1979). In this manner, a consistent set of relative thermodynamic data can be obtained which can be easily recalculated when better data are at hand.

For each reaction we can now present two equations of equilibrium for the invariant point:

$$\begin{aligned} \Delta G_R^{P_1 T_1} = 0 = & \Delta H_R^{T_1} - T_1 \Delta S_R^{T_1} + \int_1^{P_1} \Delta V_R dP + (RT_1 \sum_1^{\hat{i}} \ln a_i)_R + \\ & + (RT_1 \sum_1^{\hat{i}} n_i \ln f_i)_R \end{aligned} \quad (14)$$

$$\begin{aligned} \Delta G_R^{P_2 T_2} = 0 = & \Delta H_R^{T_2} - T_2 \Delta S_R^{T_2} + \int_1^{P_2} \Delta V_R dP + (RT_2 \sum_1^{\hat{i}} \ln a_i)_R + \\ & + (RT_2 \sum_1^{\hat{i}} n_i \ln f_i)_R \end{aligned} \quad (15)$$

Thus, we have a system of 2 r equations and can solve for 2 r dependent variables. For each reaction we can subtract equation (14) from equation (15).

$$\begin{aligned}
\Delta G_R^{P_2 T_2} - \Delta G_R^{P_1 T_1} = 0 &= \Delta H_R^{T_2} - \Delta H_R^{T_1} - T_2 \Delta S_R^{T_2} + T_1 \Delta S_R^{T_1} + \\
&+ \int_1^{P_2} \Delta V_R dP - \int_1^{P_1} \Delta V_R dP + (RT_2 \sum_1^i n_i \ln f_i)_R - \\
&- (RT_1 \sum_1^i n_i \ln f_i)_R + (RT_2 \sum_1^i \ln a_i)_R - (RT_1 \sum_1^i \ln a_i)_R
\end{aligned} \quad (16)$$

If we consider ΔV_R independent of pressure and since

$$\Delta H_R^T = \Delta H_R^{T_0} + \int_{T_0}^T \Delta C_p^R dT \quad (17)$$

$$\Delta S_R^T = \Delta S_R^{T_0} + \int_{T_0}^T \frac{\Delta C_p^R}{T} dT \quad (18)$$

$$\text{and } (\sum_1^i n_i \ln f_i)_R + (\sum_1^i \ln a_i)_R = \ln K_R \quad (19)$$

we can reduce expression (16).

$$\begin{aligned}
0 &= \int_{T_1}^{T_2} \Delta C_p^R dT - (T_2 - T_1) \Delta S_R^{T_1} - T_2 \int_{T_1}^{T_2} \frac{\Delta C_p^R}{T} dT + (P_2 - P_1) \Delta V_R + \\
&+ RT_2 \ln K_R^{P_2 T_2} - RT_1 \ln K_R^{P_1 T_1}
\end{aligned} \quad (20)$$

When the above-mentioned conditions are fulfilled, $\Delta S_R^{T_1}$ for each reaction can be solved by equation (20) and then $\Delta H_R^{T_1}$ by equation (14).

The phase rule

$$C + 2 = P + F \quad (21)$$

specifies the number of phases present as a function of the number of components and the degree of freedom. In a P-T-X volume, we have one degree of freedom and C+1 phases at an isobaric invariant point. Since by definition

$$\Delta H_R^T = \sum_1^i n_i \Delta H_i^T (\text{products}) - \sum_1^i n_i \Delta H_i^T (\text{reactants}) \quad (22)$$

and

$$\Delta S_R^T = \sum_1^i n_i \Delta S_i^T \text{ (products)} - \sum_1^i n_i \Delta S_i^T \text{ (reactants)} \quad (23)$$

we can elucidate the relative ΔH_i^f and ΔS_i^f of the phases, if the number of reaction curves from the invariant point is one less than the number of phases.

$$r = p - 1 = C \quad (24)$$

In this case, we can define one pair of $(\Delta H_i^f, \Delta S_i^f)$ as independent variables and calculate the dependent pairs by equations (22) and (23). If degenerate reactions are passing through the investigated invariant point, then additional pairs of $(\Delta H_i^f, \Delta S_i^f)$ must be defined as independent variables. These new pairs must be consistent with the former.

Summary

This new 'interstratified buffering' technique promises to speed up work in retrieving reliable and consistent thermodynamic data. It is also possible to work with complicated systems having many components as long as the compositions of participating phases are known by analysis of reaction products or retrieval of data from invariant parageneses discovered in the field.

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